(5) S. Kapf and C. Paal, *Chem. Ber.*, **21**, 3061 (1888).
(6) The 2,5-diphenyl-1-pyrrolyl radical might be converted to **11** by hydrogen transfer to nitrogen and/or by hydrogen abstraction to give 2,5-diphenyl-3*H*-pyrrole and then hydrogen migration.

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Received July 11, 1978

Structure and Origin of the Onion Lachrymatory Factor. A Microwave Study[1-3]

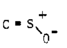
Sir:

A variety of structures have been proposed for the lachrymatory factor (LF) of the onion (*Allium cepa*) since the molecular formula C_3H_6SO was first determined in 1956[4] and the cellular precursor *trans*-(+)-*S*-(1-propenyl)-L-cysteine sulfoxide (**1a**) identified in 1961.[5] Among the possibilities

$RS(O)CH_2CH(NH_2)COOH$
1a R = E-CH_3CH=CH
b R = CH_2=CH
c R = $CH_3CH_2CH_2$

$HOCH_2CH_2CHS$ **2**

(E)-CH_3CH=CHS(O)H **3**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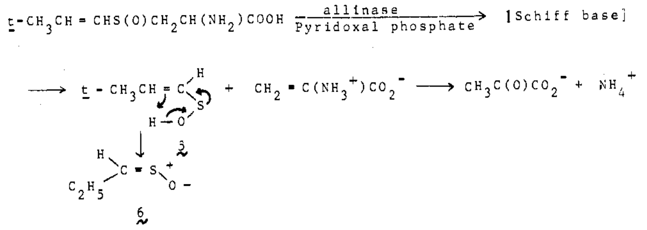
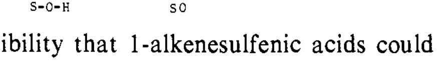
suggested for the LF have been β-hydroxypropanethial (**2**),[4] (*E*)-1-propenesulfenic acid S–H tautomer (**3**),[6] (*E*)-propanethial *S*-oxide (**4**),[7] and an interconverting mixture of the latter two structures.[10] Recently we reported the application of flash vacuum pyrolysis (FVP) spectroscopic approaches to the study of structures related to **2–4**, namely thioformaldehyde, CH_2S,[13] methanesulfenic acid, CH_3SOH,[14] and sulfine, CH_2SO.[2] We now report the application of microwave (MW) and FVP-MW techniques to the characterization of the onion LF, for which we report a revised structure together with a unifying proposal for its genesis. We also report a new synthesis of sulfines discovered during the course of these studies.

Examination by microwave spectroscopy of the LF isolated from onions[15] provided unambiguous evidence that the principal component corresponds to (*Z*)-propanethial *S*-oxide, **6**.

Scheme I

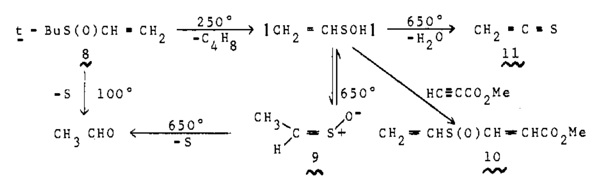


The formation of the LF **6** from precursor **1a** seems best explained by the sequence indicated in Scheme I.[16] It should be noted that the step linking **5** (structure preferred over **3** on the basis of the known structure of CH_3SOH[14]) and **6** requires *Z* stereochemistry in **6**, and that the conversion of **5** to **6** is analogous to the known tautomerism of thioamide *S*-oxides (eq 1).[17]

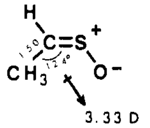

$$\mathrm{Ar\underset{\underset{S-O-H}{|}}{OC}{=}NAr'} \rightleftharpoons \mathrm{ArO\underset{\underset{SO}{\|}}{C}NHAr'} \qquad (1)$$

To test the possibility that 1-alkenesulfenic acids could rearrange to sulfines, we have examined the pyrolysis of (*E*,*Z*)-2-methyl-2-propyl 1′-propenyl sulfoxide (**7**) and 2-methyl-2-propyl vinyl sulfoxide (**8**).[18,19] We find that both **7** and **8** are efficiently converted by FVP at 250 °C to the respective sulfines **6** and (*Z*)-ethanethial *S*-oxide (**9**), as characterized by both microwave and NMR spectroscopy (see Scheme II).[15] Sulfine **9**, while not of natural origin, is likely formed by the action of onion alliinase on sulfoxide **1b**.[11] Neat **8** decomposes within 4 h at 100 °C to give, among other products, acetaldehyde which we have found to be a major decomposition product of sulfine **9**.[12] At 100 °C a solution of **8** in excess methyl propiolate affords sulfenic acid adduct **10**[19,20] (Scheme II). Finally, under FVP conditions (650–750 °C) microwave analysis indicates that sulfine **9** decomposes to both acetaldehyde and thioketene **11** (Scheme II).[21] We postulate that at these high temperatures **9** is in equilibrium with ethenesulfenic acid which undergoes dehydration to thioketene.[22]

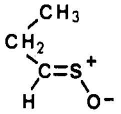
Scheme II

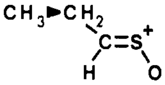


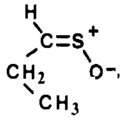
The structures of (*Z*)-ethanethial *S*-oxide (**9**) and (*Z*)-propanethial *S*-oxide (**6**) were determined through analysis of the microwave spectra of the respective normal isotopic species. Since rotational constants are available only for a single isotopic species for each, structural conclusions are based upon the assumption that the -CHSO framework is the same as that of sulfine[2] and that the methyl group are tetrahedral with C–H = 1.093 Å. For **9** a structure fit to the observed rotational constants (with the above constraints) gives C–C = 1.50 Å, ∠CCS = 124°, a *Z* (syn) CCSO arrangement, a dipole moment of 3.33 (2) D, and a CH_3 internal rotation barrier of 0.8 kcal mol^{-1}. There is no microwave evidence for the presence of the *E* (anti) isomer of **9**.

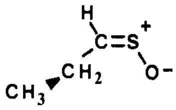


9


4a


4b


6a


6b

For propanethial *S*-oxide **4** or **6**, without multiple isotopic substitution, only the overall molecular conformation can be determined with certainty. Internal rotation about the CH–CH_2 bond gives this sulfine an additional conformational degree of freedom with the four most likely conformations being *Z* cis (**6a**), *Z* skew (**6b**), *E* cis (**4a**), and *E* skew (**4b**). Assuming the ethanethial *S*-oxide framework determined above, and C–CH_3 = 1.525 Å and ∠CCC = 109.5°, the rotational constants for the four likely conformers **4a**, **4b**, **6a**, and **6b** have been calculated and compared with the observed constants. Only **6b** and **4a** have rotational constants similar to the observed values and of these two only the *Z*-skew rotamer **6b** fulfills the heavy-atom nonplanarity implied by the observed constants. The torsional angle about the CH–CH_2 bond which best reproduces the observed *Z*-skew **6b** rotamer's rotational constants is ~125° (displaced from methyl, S=O cis as in **6b′**), but is uncertain by an estimated ±10° owing to the many structural assumptions involved. The intense torsional satellite

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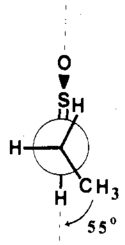

spectra of (*Z*)-propanethial *S*-oxide (**6**) suggest that the preference for the skew conformation is not a very strong one. Unlike the parent sulfine,[2a] sulfines **6** and **9** are stable in the waveguide at 50 mTorr and 25 °C. It has not yet proven possible to observe directly by microwave spectroscopy (or other spectral means) 1-alkenesulfenic acids either in the pyrolysis of **7** or **8** or in the vapors or extract from homogenized onions.

Careful FT NMR analysis of the isolated onion LF as well as the sulfines from pyrolysis of alkenyl sulfoxides **7** and **8** reveals the presence in each case of a minor (<10%) component characterized as the (*E*)-sulfine (e.g., **4** from the onion and from **7**). Details of this work will be presented elsewhere.

Acknowledgment. Support for this research from the Research Corporation (R.E.P.), the donors of the Petroleum Research Fund, administered by the American Chemical Society (E.B.), the North Atlantic Treaty Organization Research Grants Programme (E.B.), and the University of Missouri—St. Louis is gratefully acknowledged. We thank Professor Frank Davis for helpful discussion and Mr. Ali Bazzi for technical assistance.

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(7) In the literature dealing with the onion LF there is no specific mention of the possibility of geometric isomers for propanethial *S*-oxide despite the extensive research on geometric isomerism in thiocarbonyl *S*-oxides.[8] In some studies propanethial *S*-oxide is depicted with a linear CSO grouping devoid of any stereochemistry,[9,10] while in other papers an *E* stereochemistry is somewhat arbitrarily indicated.[11,12]
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(15) Details of the isolation and an FT NMR study of the onion LF and related alkanethial *S*-oxides will be described elsewhere.
(16) The salient points on which we base our conclusions are the following. (a) The onion enzyme alliinase converts sulfoxide **1c** to *n*-propyl propanethiosulfinate, a process which likely involves the intermediacy of propanesulfenic acid.[14] (b) When the LF is generated in D_2O the M^+ ion in its mass spectrum shifts from 90 to 91 indicating a single exchangeable proton.[6] The monodeuterio LF loses OH rather than OD on electron impact.[6] Since methanesulfenic acid is known to have the exchangeable hydrogen on oxygen,[14] which form should readily lose OH on electron impact, rearrangement of the monodeuterio LF must precede fragmentation. (c) The *direct* formation of the LF **6** from precursor **1a** is postulated to involve a retro-ene reaction.[11] It would be remarkable if the same enzyme alliinase could catalyze both the sulfoxide elimination reaction described in (a) above as well as a retro-ene process with **1**. (d) An alternative mechanism from **1a** to **6** which we cannot exclude at this time would involve elimination from the Schiff base of Scheme I giving the anion of acid **5** which could directly give **6** on protonation of the appropriate resonance form.
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(18) Prepared by oxidation of the corresponding known sulfide or via reaction of the alkenyl Grignard reagent with 2-methyl-2-propanesulfinyl chloride.
(19) All new compounds have been fully characterized by spectral methods.
(20) For examples of addition of α,β-unsaturated (and other) sulfenic acids to alkynes, see Block, E.; O'Connor, J. *J. Am. Chem. Soc.* **1974,** *96*, 2931–3928, 3929–3944. For an example of an intramolecular addition of an α,β-unsaturated sulfenic acid, see Baxter, A. G. W.; Stoodley, R. J. *J. Chem. Soc., Chem. Commun.* **1976,** 366–367.
(21) The microwave spectrum of thioketene has been reported by Kroto: Georgiou, K.; Kroto, H. W.; Landsberg, B. M. *J. Chem. Soc., Chem. Commun.* **1974**, 739–740.
(22) We have also observed that methanesulfenic acid on FVP undergoes dehydration to thioformaldehyde[14] and that methyl vinyl sulfide on FVP (at 770 °C) gives thioketene. These reactions may all involve mechanistic pathways similar to those proposed by Kwart for other gas phase thermolytic β-eliminations.[23]
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Received September 19, 1978

Photochemical Reaction of Dicyanoanthracene with Acetonitrile in the Presence of an Aliphatic Amine. A Novel Photochemical Amination

Sir:

Photochemical reactions involving electron transfer followed by proton transfer are well examined on arene-amine systems.[1] For instance, irradiation of a solution of anthracene and a secondary amine in acetonitrile yielded both the 1:1 adducts and the reduction products of anthracene.[2] We now report that irradiation of 9,10-dicyanoanthracene (**1**), a more powerful electron acceptor than anthracene itself, in acetonitrile in the presence of a primary, secondary, or tertiary amine did not yield the 1:1 adduct of the amine and **1** but reaction products between **1** and acetonitrile.

Irradiation of a mixture of **1** (70 mg) and butylamine (20 mL) in acetonitrile (300 mL)[3] with a Pyrex-filtered medium-pressure mercury arc (100 W) for 4 h under nitrogen gave 9-amino-10-cyanoanthracene (**2**), mp 259–260 °C (lit.[4] mp 262–263 °C), *m/e* 218 (M^+), in 64% yield. Acetaldehyde and butyraldehyde were also identified in the reaction mixture as the corresponding 2,4-dinitrophenylhydrazones. A similar result was obtained when **1** in the acetonitrile[3] was irradiated in the presence of diethylamine or triethylamine producing **2** in 42 or 34% yield together with acetaldehyde, respectively.

To clarify the origin of the nitrogen in the amino group of **2**, we carried out similar photochemical reactions of **1** in 90% aqueous acetonitrile-^{15}N (96.9 atom %) in the presence of triethylamine. The mass spectra clearly showed that the major product (>95%) was ^{15}N-incorporated **2.** This result explicitly indicates that the nitrogen in the amino group of **2** originates from the acetonitrile. In accord with this result, when methanol or benzene was substituted for acetonitrile, 9-cyanoanthracene

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